PB88-186846

Interlaboratory Comparison of Formaldehyde Emissions from Particleboard Underlayment in Small-Scale Environmental Chambers

Acurex Corp., Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

1987

U.S. Department of Commerce
National Technical Information Service

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completi

1. REPORT NO. EPA/600/J-87/303	2.	3. PB88-186846
4. TITLE AND SUBTITLE Interlaboratory Comparison of Formaldehyde Emissions from Particleboard Underlayment in Small-scale Environmental Chambers (Journal Version)		5. REPORT DATE 1987 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) T. Matthews, D. Wilson, A. Thompson (ORNL); and M. Mason, S. Bailey, L. Nelms (Acurex)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Acurex Corporation * P.O. Box 13109 Research Triangle Park, North Carolina 27709		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. EPA 68-02-3988 and IAG DW89930762-01-4
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Journal Article; 9/86-6/87 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is Bruce A. Tichenor, Mail Drop 54, 919/541-2991. JAPCA 37: 1320-1326 (1987). Research at ORNL (EPA IAG) under DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. (*)

16. ABSTRACT The paper gives results of measurements of formaldehyde (CH_2O) emissions from particleboard underlayment in 0.17 and 0.2 cu m chambers at separate laboratories to test the comparability of small scale environmental chamber measurements under different ventilation and product loading conditions. Absolute CH_2O calibration was established through intermethod comparison of different monitoring techniques against a CH_2O generation apparatus. Interlaboratory precision was enhanced via co-calibration of each laboratory's CH_2O colorimetric analyzer against the same blank and bi-level generation source at the beginning and end of the study. The results show excellent intermethod and interlaboratory agreement in both the CH_2O calibration and particleboard emissions testing. The CH_2O emission rates of the test specimens demonstrate a Fick's Law dependence on CH_2O vapor concentration. Measured CH_2O concentrations are described by a single-compartment, single-emitter model, and are inversely proportional to the ratio of the air exchange rate and product loading. (Copyright (C) 1987 JAPCA.)

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Ventilation	Pollution Control	13B	13A
Formaldehyde	Loading	Stationary Sources	07C	
Emission	Colorimetric Analysis	Indoor Air	14G	07D
Measurement			14B	
Particle Boards			11G	
Test Chambers				

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified 20. SECURITY CLASS (This page) Unclassified	21. NO. OF PAGES 9 22. PRICE PC $9.95/MF $6.95

EPA Form 2220-1 (9-73)

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
SPRINGFIELD, VA. 22161

JAPCA 37: 1320–1326 (1987)

EPA/600/J-87/303
JOURNAL ARTICLE

Interlaboratory Comparison of Formaldehyde Emissions from Particleboard Underlayment in Small-Scale Environmental Chambers

T. G. Matthews, D. L. Wilson and A. J. Thompson
Oak Ridge National Laboratory
Oak Ridge, Tennessee

M. A. Mason, S. N. Bailey, and L. H. Nelms
Acurex Corporation
Research Triangle Park, North Carolina

Formaldehyde (CH_2O) emissions from particleboard underlayment have been measured in 0.17 and 0.2 m^3 chambers at separate laboratories to test the comparability of small scale environmental chamber measurements under different ventilation and product loading conditions. Absolute CH_2O calibration was established through intermethod comparison of different monitoring techniques against a CH_2O generation apparatus. Interlaboratory precision was enhanced via co-calibration of each laboratory's CH_2O colorimetric analyzer against the same blank and bi-level generation source at the beginning and end of the study. The results show excellent intermethod and interlaboratory agreement in both the CH_2O calibration and particleboard emissions testing. The CH_2O emission rates of the test specimens demonstrate a Fick's Law dependence on CH_2O vapor concentration. Measured CH_2O concentrations are described by a single-compartment, single emitter model, and are inversely proportional to the ratio [N/L (m/h)] of the air exchange rate [$N(h^{-1})$] and product loading [$L(m^{-1})$]. Comparison tests at varying N and L, but uniform N/L were performed; similar CH_2O concentrations were measured for N and L levels selected from an indoor compartment model, and for fivefold larger N and L values, which are more convenient for small-scale chamber testing.

Environmental test chambers are important tools for characterizing organic emissions from consumer and construction products and evaluating their potential impact on indoor air quality.[1] The emission potential of carefully selected products can be investigated as a function of environmental, ventilation, product use, and product loading [i.e., product surface area (m^2)/compartment volume (m^3)] parameters. The physical design of the test chamber should be developed considering (1) requirements for controlled product exposure and testing, and (2) the limitations of chambers of varying design (e.g., size and wall composition).

The selection of a comparatively large-scale (e.g., walk-in) or small-scale (e.g., <1 m^3) test chamber involves tradeoffs in experimental capability whose consequences vary with study objectives.[1] Large-scale chambers (LSCs) provide a closer simulation of indoor compartments because emission sources, air exchange rates, air mixing patterns, and product use parameters can be directly scaled to real-world scenarios (e.g., Reference 2). Disadvantages of LSCs include cost and reduced measurement flexibility; operation at controlled, low air exchange levels, for example, can be hampered by leakage to the surrounding atmosphere. Small-scale chambers (SSCs) provide a complementary measurement capability to LSCs. Emissions data from many specimens can be taken under a range of environmental and ventilation conditions at comparatively reduced cost. However, precise scaling of real-world compartments in SSCs can lead to unacceptably low air flow rates and product areas or mass. The test specimens can be too small to adequately represent nonhomogeneous products.[3,4] The limitations of SSCs is an area of active research and is a primary concern of this study.

Formaldehyde (CH_2O) emissions from pressed-wood products, particularly particleboard underlayment, and its dependence on product loading and ventilation parameters have been extensively studied and modeled (e.g., References 2,5–7). A single-compartment treatment of Hoetjer *et al.*[8] describing common environmental chamber tests yields

$$[CH_2O]^{-1} = \{[CH_2O]_{eq} \cdot K\}^{-1} \cdot N/L + [CH_2O]_{eq}^{-1} \quad (1)$$

where:

$[CH_2O]$ = the CH_2O concentration ($\mu g/m^3$) inside the chamber at some N/L,
$[CH_2O]_{eq}$ = the equilibrium CH_2O concentration ($\mu g/m^3$) at zero air exchange,
K = the CH_2O mass transport coefficient (m/h) of the test product, and
N/L = the air exchange (h^{-1}) to product loading [area (m^2)/volume (m^3)] ratio (m/h).

Given the simplifying assumptions of a single emitter, a single compartment with uniform mixing, and no CH_2O losses due to air filtration or sinks, the steady-state CH_2O concentration is inversely proportional to N/L. This model suggests that N and L levels may be scaled higher for convenient SSC testing of inhomogeneous products yet maintain real-world N/L values. The limitations of this model in SSC testing are an additional concern of this study. Correlations between SSC and LSC experiments at common N/L may be limited to specific ranges of N and L as a function of test product.[4]

The spatial uniformity of CH_2O emissions from pressed-wood products has been studied in a survey of contemporary materials.[9] Although potentially large intermanufacturer variation in CH_2O emission strength is indicated, comparatively small intraboard variation is observed. The average coefficient of variation for combined intraboard variation and measurement uncertainty (i.e., assuming a 0.032 m^2

Copyright 1987—APCA

sampling area) ranged only from 12 percent for medium density fiberboard to 22 percent for print, hardwood-plywood paneling. In practice, decreases in SSC test precision due to intraproduct inhomogeneity can be minimized by cutting specimens from multiple regions of large product samples.

An interlaboratory comparison of CH_2O emissions from a selected particleboard underlayment in SSC tests has been performed to investigate practical limits of precision under varied N, L, and N/L conditions. To minimize interlaboratory imprecision, specimen preparation and preliminary conditioning were performed by a single laboratory. Calibration and measurement protocols were standardized. In addition, product specimens were exchanged between laboratories at the midpoint of the study to minimize the impact of interspecimen variation and sample mailing. The overall test period was also kept brief (i.e., 1.5 months) to minimize product aging affects. The results of this study should encourage continued method development for broader SSC testing of organic emitters.

Experimental Design

The experimental methods and design used in this study can be broken down into five components: preparation and conditioning of test specimens; environmental chamber design; calibration and control of measurement parameters; selection of environmental, air exchange, and product loading parameters; and finally, test protocols for measurement of CH_2O emissions from the specimens of particleboard underlayment.

Preparation and Conditioning of Test Specimens

The particleboard underlayment sample was originally purchased from a retail store in 1984[10] and stored under laboratory conditions through October 1985. Particleboard specimens were then trimmed to an area of 0.065 m^2 (i.e., about 0.014 × 0.023 m) and edge coated with $NaSiO_4$. Three brush coats of $NaSiO_2$ yielded an approximate tenfold reduction in CH_2O emissions. Traditional metallic tape or paraffin coatings could not be used because of concurrent chamber studies investigating a spectrum of volatile organic emissions.[11] The test specimens were then collectively conditioned at ORNL at 23 ± 1°C, 50 ± 3 percent RH and <250 $\mu g/m^3$ CH_2O for two months prior to CH_2O emissions testing.

Chamber Design

The physical designs of the EPA and ORNL SSCs were similar but with significant differences. The interior volumes and surface compositions were 0.167 m^3 and stainless steel for the EPA chamber, and 0.206 m^3 and Teflon for the ORNL chamber. Air inlets to- and exhausts from- the EPA and ORNL SSCs had combined areas of approximately 0.32 and 1.27 cm^2, respectively to ensure similar, small, pressure differentials across the chambers. Air entered the EPA SSC through a single portal and exhausted through a single portal to a secondary one-liter mixing flask followed by a sampling manifold. To enhance mixing in the ORNL SSC, supply air was diffused into four separately directed streams inside the SSC and exhausted through eight portals distributed around the SSC into a one-liter sampling manifold. Additional mixing inside both EPA and ORNL SSCs was accomplished with miniature, low-speed fans. Metallic sample holders were used in both SSCs to uniformly separate and position particleboard specimens about the geometric center of the SSC.

Calibration and Experimental Control Methods

Extensive calibration was performed to verify measurements of temperature (T), relative humidity (RH), and air flow rate, inside the SSCs. Temperature was measured using a thermometer in the ORNL SSC and a thermocouple in the EPA SSC; both were calibrated against the same NBS thermometer (i.e., ±0.1°C). Temperature was automatically controlled by housing each SSC inside a larger temperature-regulated chamber. In the ORNL SSC, RH was measured using a hygrometer calibrated against wet/dry bulb measurement devices (i.e., ±2–3 percent RH); RH was controlled via operator adjustment of a bubbler in-line with the chamber supply air. In the EPA SSC, RH was measured using an electrochemical sensor calibrated against headspace vapors from saturated NaCl and LiCl solutions; RH was controlled using a syringe pump in-line with the SSC supply air. Air flow rates were controlled by mass flow valves calibrated against a wet test meter at ORNL and soap bubble flowmeters at EPA. The wet test meter was calibrated against NBS-traceable, differential-pressure, measurement devices (i.e., ±1 percent).

Calibration for monitoring of CH_2O vapor concentration involved extensive intermethod and interlaboratory comparisons to enhance both measurement accuracy and precision. CEA instruments[12] were used by both laboratories according to published protocols[13] for all particleboard emissions testing. Both CEA instruments were calibrated at ORNL against the same source of CH_2O vapor at approximate 0 (i.e., supply air), 90 and 190 $\mu g/m^3$ concentrations prior to the start and following the completion of the particleboard emissions testing. Formaldehyde vapor was generated by injecting dilute formalin solution into a humidified and heated air stream that was cooled before entering the SSC.[14] Unless otherwise noted, a 10 L/min air flow was used to provide ample CH_2O vapor for sampling by multiple instruments. The generated CH_2O vapor concentration was calculated from (1) the measured air flow rate, (2) a gravimetric measurement of the injected solution per unit time, and (3) the CH_2O concentration in the injected solution.[13] The concentration of the injection solution was determined from a precise dilution of a potentiometrically titrated stock solution of approximately 4000 μg CH_2O/mL H_2O. Generated CH_2O vapor was independently measured with a refrigerated, triple-impinger, air-sampling unit, using distilled, deionized water as a CH_2O sorbent. A 98 percent CH_2O collection efficiency was achieved. The CH_2O–H_2O samples were analyzed following 8–24 h sampling periods using a modified pararosaniline colorimetric analysis.[13] This method was standardized against approximate 0, 0.5, and 1.0 μg CH_2O/

Table I. Summary of experimental parameters selected for particleboard emissions testing.

Test series	Number specimens	Air flow rate (L/min)	Surface area (m^2)	N (h^{-1})		L (m^{-1})*		N/L (m/h)
				EPA	ORNL	EPA	ORNL	
1	1	1.5	0.065	0.54	0.44	0.39	0.32	1.38
2	2	10.0	0.130	3.61	2.91	0.78	0.63	4.62
3	5	7.5	0.325	2.71	2.18	1.96	1.58	1.38
4	3	1.5	0.195	0.54	0.44	1.17	0.95	0.46

* Specimen area (m^2)/chamber volume (m^3).

Table II. Joint EPA-ORNL calibration summary. Average CH_2O concentrations ($\mu g/m^3$) determined for common sources of CH_2O vapor at about 90 and 190 $\mu g/m^3$.

Date	Generation apparatus	CEA Instruments[a] ORNL	CEA Instruments[a] EPA	Aqueous impinger	DNPH sampler
		A. Phase I calibration data			
1/6	99	100 ± 4	97 ± 3	98 ± 4	—
1/7	98	104 ± 5	104 ± 2	109 ± 6	—
	190 ± 4	194 ± 5	189 ± 9	189 ± 9	—
1/8	98	—	—	95 ± 6	107 ± 2
	190	—	—	186 ± 7	195
		B. Phase II calibration data			
2/25	98	100 ± 6	100 ± 6	103 ± 5	—
	191	177 ± 3	179 ± 3	184 ± 3	—
2/26	97	102 ± 4	99 ± 3	94 ± 2	—
(day)	192	186 ± 3	179 ± 6	145 ± 31[b]	—
2/26	96	100 ± 6	101 ± 3	101 ± 0	—
(night)	190	194 ± 3	193 ± 3	191 ± 2	—

[a] The Phase I CEA calibrations were 7.2 ± 0.3 and 4.6 ± 0.2 mv/($\mu g/m^3$ CH_2O) for the EPA and ORNL instruments, respectively. Phase II calibrations were correspondingly 6.7 ± 0.03 and 4.2 ± 0.2 mV/($\mu g/m^3$ CH_2O).

[b] Data rejected from calibration due to suspected experimental error.

mL H_2O solutions prepared from potentiometrically-titrated, 4000 μg CH_2O/mL H_2O stock solution. The average of the CH_2O vapor concentrations calculated for the CH_2O generation system and determined from the impinger/colorimetric analysis was used to calibrate the response of both CEA instruments. Additional checks of the CH_2O generation system and selected particleboard emissions tests were performed using dinitrophenylhydrazine (DNPH) coated silica gel cartridges with subsequent high pressure liquid chromatographic analysis.[15] This CH_2O analysis technique is calibrated against quantitatively-diluted, CH_2O-hydrazine derivative solutions.

Selection of Test Conditions

All particleboard emissions testing was performed at 23°C and 50 percent RH. Air exchange rates and particleboard loadings were selected on the basis of a single compartment model of Matthews *et al.*[5] and Equation 1. A 4 × 4 × 2.5 m (i.e., 40 m^3) compartment is assumed with an effective CH_2O emitting area of 8 to 16 m^2 due to particleboard underlayment. The impact of product use parameters such as the CH_2O permeability of decorative flooring materials were not considered. The air exchange rate is assumed to vary between 0.2 and 1.0 h^{-1}, yielding a tenfold range of possible N/L values between 0.5 and 5.0 m/h. The selection of experimental values thus included N/L values from 0.46 to 4.6 m/h. Dual tests at N/L = 1.38 but with varying N and L values were also performed to evaluate the constancy of the N/L term in Equation 1. A summary of the experimental test conditions is given in Table I.

Protocol for CH_2O Emissions Testing

The schedule for CH_2O calibration, and product conditioning and testing was carefully defined in a QA/QC plan prior to the start of experimental studies. The particleboard specimens were first randomly divided into X and Y board sets. During phase I of the study, CH_2O analyzers were jointly calibrated at ORNL, followed by product testing of the X board set at ORNL and Y board set at EPA. Product specimens from both labs were returned following testing to a single conditioning chamber at ORNL. In Phase II of the study, X and Y board sets were exchanged between laboratories and retested. A joint CH_2O calibration at ORNL concluded experimental studies. Different lot numbers of para-

Table III. Intermethod comparisons performed during product emission testing. Average CH_2O concentrations determined for the same sources of CH_2O vapor.

Date	CH_2O source	Test series	Air flow rate (L/min)	Generation apparatus	Impinger	CEA instrument	DNPH
				A. ORNL data			
1/14	board	3	7.5	—	123 ± 3	124 ± 6	—
1/17	gener.	—	1.5	123 ± 3	118 ± 12	—	—
	board	4	1.5	—	244[a]	193 ± 6[a]	—
1/20–	board	1	1.5	—	131[a]	116 ± 7[a]	—
1/21	board	2	10.0	—	52 ± 4	47 ± 3	—
1/27	board	4	1.5	—	215[a]	172 ± 6[a]	—
	board	4	1.5	—	198[a]	190 ± 5[a]	—
2/4	gener.	—	10.0	190	187 ± 8	195 ± 9	—
	board	3	7.5	—	131 ± 1	136 ± 7	—
2/7	gener.	—	10.0	186 ± 5	189 ± 5	193 ± 9	—
	board	4	1.5	—	215[a]	220 ± 8[a]	—
2/11	board	1	1.5	—	127[a]	116 ± 2.6	—
	board	2	10.0	—	46 ± 5	47 ± 2	—
2/13–	board	1	1.5	—	113[a]	118 ± 1[a]	—
2/14	board	1	1.5	—	92[a]	92 ± 4[a]	—
				B. EPA data			
2/18	board	2	10.0	—	—	50 ± 2	51

[a] Intermethod comparisons were sequential in time. Concurrent measurements were impossible due to the low air flow rates.

rosaniline reagent were used in Phase I and II of the study. As a result, the initial and final joint calibrations were used independently with Phase I and II product emissions data.

Prior to CH_2O emissions testing, product specimens were transferred from the collective conditioning chamber at ORNL to SSCs for about 48 h of additional conditioning at 23°C, 50 percent RH and specified N and L levels. Test specimens were positioned on the sample holder to maximize specimen-specimen and specimen-wall separation, thereby enhancing the mixing within the SSC. Formaldehyde measurements (i.e., about 15 min long) were repetitively cycled between the exhaust from the SSCs and blank filtered air to correct for the time varying baseline of the CEA instrument.[12,13] At each N/L test condition, alternating blank and SSC measurement cycles were conducted typically three and 10–25 times by EPA and ORNL, respectively. All experimental CH_2O calibration and particleboard emissions data taken with the CEA instruments are reported as the mean ± S.D. of these blank-corrected, SSC measurement cycles.

tion and impinger/colorimetric analysis methods over an entire joint calibration series.

Additional intermethod comparisons were performed concurrent with Phase I and II product emissions work to test the temporal stability of the CH_2O calibrations (see Table III). In contrast to the joint calibration series (Table II), two sources of CH_2O vapor (i.e., particleboard and dilute formalin solution) and a range of 1.5 to 10.0 L/min air flow rates were used. Potential concerns at low flow rates include increased sorption of CH_2O vapor on the chamber walls and insufficient air flow for concurrent intermethod comparisons.

The results given in Table III indicate consistently good intermethod agreement with the exception of the Series 4 measurements of particleboard underlayment at 1.5 L/min on 1/17 and 1/27. Intermethod discrepancies are typically < 5–10 percent. No explanations concerning the aberrant Series IV data are readily apparent because other Series 4 and Series I measurements at 1.5 L/min show good intermethod agreement. Intermethod discrepancies of <5 percent are

Table IV. Particleboard CH_2O emissions data. Summary of average N/L (m/h), CH_2O concentration ($\mu g/m^3$) and CH_2O emission rate [CH_2OER ($\mu g/m^2h$)] values.

Test series	Specimen number	EPA results			ORNL results		
		N/L	$[CH_2O]$	CH_2OER	N/L	$[CH_2O]$	CH_2OER
			A. X Board Set				
1	1	1.31	108 ± 6	140 ± 8	1.38	109 ± 2	150 ± 3
1	2	—	—	—	1.38	127 ± 7	175 ± 9
1	3	—	—	—	1.38	115 ± 7	159 ± 9
2	1,2	4.50	50 ± 3	226 ± 10	4.58	47 ± 3	216 ± 15
3	1,2,3,4,5	1.37	105 ± 5	144 ± 7	1.38	124 ± 6	172 ± 8
4	1,2,3	0.43	207 ± 11	90 ± 5	0.46	190 ± 6	88 ± 3
4	4,5,6	—	—	—	0.46	172 ± 6	79 ± 2
			B. Y Board Set				
1	1	1.33	105 ± 1	140 ± 2	1.38	117 ± 1	162 ± 2
1	2	—	—	—	1.38	92 ± 4	126 ± 5
1	3	—	—	—	1.38	115 ± 3	159 ± 4
2	1,2	4.51	53 ± 4	240 ± 18	4.58	47 ± 2	212 ± 7
3	1,2,3,4,5	1.36	121 ± 16	165 ± 21	1.38	133 ± 3	183 ± 4
4	1,2,3	0.45	230 ± 12	103 ± 5	0.46	217 ± 8	100 ± 4

Results and Discussion

Formaldehyde Calibration Data and Intermethod Comparisons

The results of the EPA-ORNL joint CH_2O calibration work with common sources of about 90 and 190 $\mu g/m^3$ CH_2O are summarized in Table II by individual CH_2O vapor generation experiments. Brief interruptions between the typically 8–24 h CH_2O generation sessions were required to weigh and refill the injection syringe with dilute formalin solution. During these interruptions, the air flow to the chambers was shut off to minimize dilution of CH_2O vapor inside the SSCs. Each comparison of CH_2O monitoring techniques summarized in Table II involves a strong temporal overlap during the operation of the CH_2O generation system.

Both Phase I and Phase II calibration results (Table II) show good intermethod agreement between mean CH_2O vapor concentrations. Discrepancies are typically < 5–10 $\mu g/m^3$. This is important because the results of the CH_2O generation system, aqueous impinger/colorimetric analyses and DNPH sampler/chromatographic analyses represent near-independent determinations of CH_2O concentration, tied only to a common 4000 $\mu g/mL$ formalin standard. The CEA concentration data are more strongly tied to the results of the CH_2O generation system and impinger/colorimetric analysis methods. CEA calibration factors [i.e., $mV/(\mu g/m^3\ CH_2O)$] are determined from the mean result for the generation apparatus and also observed between the CH_2O other analytical methods at both 1.5 and 10.0 L/min flow rates. This indicates a minimal sink effect at these flow rates, at least in the ORNL Teflon-lined chamber. In summary, no significant changes in intermethod calibrations are observed with time in Phase I or II particleboard testing, or as a function of air flow rate to the SSCs.

Particleboard Emissions Data

The particleboard CH_2O emissions data are summarized in Table IV by laboratory, test series (see Table I), X and Y board set, and specimen number to facilitate a variety of intercomparisons among the data. Generally good interlaboratory agreement in CH_2O emissions are observed between equivalent test series and test specimens; considering both X and Y board sets, interlaboratory discrepancies in the mean CH_2O concentrations range from 1 to 19 $\mu g/m^3$, averaging only 10 $\mu g/m^3$. Regression of the mean CH_2O emission rate data for EPA board sets X and Y against the ORNL results for identical product specimens (see Figure 1) yields slope and intercept values of 1.07 ± 0.16 and −15 ± 26 $\mu g/m^2h$, respectively. Consistent with previously reported studies,[9] interspecimen (i.e., intraboard) variation in CH_2O emissions is fairly small. Considering ORNL Test Series 1 data (i.e., single board tests) for both X and Y board sets, the mean CH_2O concentrations range from 92 to 127 $\mu g/m^3$, averaging 113 ± 12 $\mu g/m^3$. Thus, interlaboratory variation in

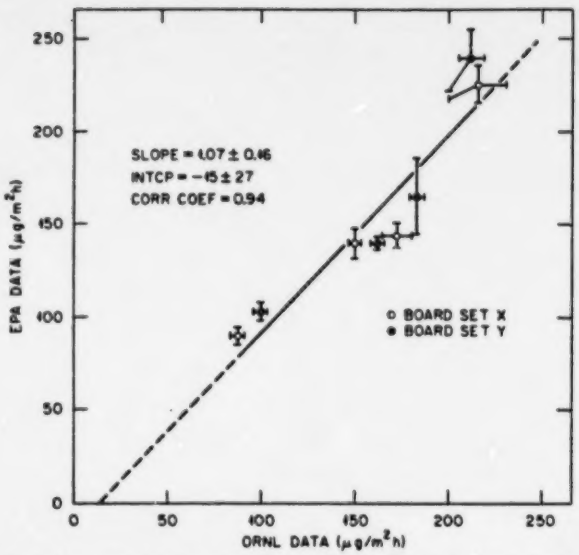

Figure 1. Interlaboratory linear regressions of mean CH_2O emission rates ($\mu g/m^2h$) calculated from EPA and ORNL measurements of common product specimens.

calibration and experimental protocol may contribute less to measurement imprecision than interspecimen variation in CH_2O emission strength. Clearly several product specimens should be incorporated in SSC testing to minimize the impact of interspecimen variation in emission strength.

Comparison of the results for Test Series 1 and 3, both taken at N/L values of about 1.38 m/h, probes the utility of simple, single-compartment, single-emitter models in describing SSC experiments at uniform N/L but variable N and L levels. Test Series 1 mimics potential indoor environments with N and L values of about 0.5 h^{-1} and 0.35 m^{-1}, respectively. However, the resulting 1.5 L/min flow rate and 0.065 m^2 specimen area are inconvenient in SSC experiments. In Test Series 3, the N and L levels are both increased fivefold (see Table I). Considering both ORNL and EPA data from board sets X and Y, the average CH_2O concentrations for Test Series 1 and 3 are 111 ± 10 and 121 ± 12 $\mu g/m^3$, respectively. The slightly lower results for Test Series 1 would be consistent with increased wall (i.e., sink) effects at the low 1.5 L/min air flow rates. These results support the single-compartment, single-emitter model expressed in Equation 1 and suggest that N and L values may be scaled upward (at constant N/L) from real world scenarios to test designs more convenient for SSC testing.

Modeling of Particleboard Emissions Data

The CH_2O emissions data (i.e., Table IV) have been fit to two linear models to provide further interlaboratory comparison of the experimental results and a better understanding of important criteria in SSC test design. The mean ORNL and EPA data for Board Sets X and Y have been fit to Equation 1, which describes the variation in $[CH_2O]^{-1}$ as a function of N/L. The results show good linear fits to the model for both laboratories (see Figure 2A), and good interlaboratory agreement in regression coefficients (See Table V). Order of magnitude variation in N/L from 0.5 to 5.0 m/h (see Selection of Test Conditions) results in modeled CH_2O concentrations ranging from about 180 to 45 $\mu g/m^3$. Clearly, product loading and ventilation parameters and their potentially wide variation in indoor environments must be strongly considered in SSC test design.

A mass transport model, developed from Fick's Law of Diffusion, has been used to describe the variation of CH_2O emission rates (CH_2OER) of pressed-wood products as a function of CH_2O vapor concentration.[5]

$$CH_2OER(\mu g/m^2h) = -K(m/h) \cdot [CH_2O](\mu g/m^3) + \text{Constant} \quad (2)$$

An advantage of this treatment is that the impact of multiple CH_2O sources and CH_2O loss due to ventilation can be modeled in terms of the resulting CH_2O vapor concentration. The mean EPA and ORNL data produced reasonably linear fits to the model (see Figure 2B), and excellent interlaboratory agreement among linear regression coefficients (see Table V). The −0.75 ± 0.12 m/h slope for the combined EPA and ORNL data sets also agrees well with a reported average

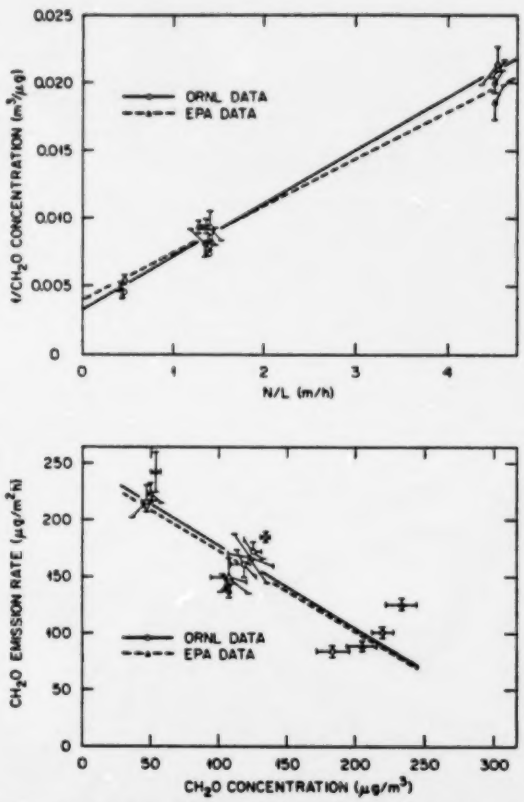

Figure 2. Fit of mean particleboard emissions data to (A) a single-compartment, CH_2O concentration model (Equation 1), and (B) a mass transport model (Equation 2). Regression lines represent the fit of the combined EPA and ORNL data sets to the models (see Table V).

slope of −0.60 ± 0.23 m/h for several different particleboard underlayments.[5] Extrapolating from this model, order of magnitude variation in CH_2O concentration from about 35 to 350 $\mu g/m^3$, observed in recent field studies,[16] results in modeled CH_2O emission rates ranging from about 210 to 0 $\mu g/m^2h$. Thus, multiple N/L test conditions and the resulting range of pollutant vapor concentrations should be strongly considered in experimental SSC test design. This is necessary to model emission processes that are pollutant concentration dependent, and to test product emission rates in a range of pollutant vapor concentrations consistent with those found in indoor environments.

Control of SSC Test Parameters

The sensitivity of measured CH_2O concentrations to interlaboratory variation in environmental, product loading and ventilation parameters is considered. Temperature was controlled to 23.00 ± 0.04°C (i.e., ± S.D.) with extremes of 22.93 and 23.06°C at EPA, and 23.08 ± 0.04°C with extremes of 22.98 and 23.11°C at ORNL. RH was controlled at 50.4 ± 1.1 percent with extremes 48.8 and 52.8 at EPA, and 49.7 ± 1.5 percent with extremes of 46.0 and 52.6 percent at ORNL. Air flow rates and product loadings were controlled within 1 to 2 percent at both laboratories. The impact of these variations on CH_2O concentrations inside the SSCs is estimated from a steady-state model of the environmental dependence of CH_2O concentrations inside a single compartment containing a single emitter.[17] The following equation describes the ratio of the CH_2O concentration at measured T, RH and N/L levels (C_T, RH, N/L) divided by the concentration at "standard" conditions of 296 K, 50 percent RH and 0.5 m/h N/L based on a combined statistical treatment of several different particleboard underlayment samples,

$$\frac{C_{V_{T,RH,N/L}}}{C_{V_{std}}} = \frac{[1 + B(T - 296)][1 + E(RH - 50)]e^{-C\left(\frac{1}{T} - \frac{1}{296}\right)}(RH/50)^A[K_{B_{std}} + 0.5]}{[1 + B(T - 296)][1 + E(RH - 50)]K_{B_{std}} + N/L} \quad (3)$$

where constants A, B, C, E, and $K_{B_{std}}$ are 0.65, 0.074, 7200, 0.015 and 0.65 (m/h), respectively.

Solving Equation 3 for test conditions of 23°C, 50 percent RH and N/L levels of 0.46, 1.38 and 4.6 m/h yields values of the ratio $C_{V_{T,RH,N/L}}/C_{V_{std}}$ that were designed for the interlaboratory comparison. Substituting experimental values for T, RH and N/L into Equation 3 then yields comparative values of $C_{V_{T,RH,N/L}}/C_{V_{std}}$, reflecting the deviations from study design. Holding RH constant at 50 percent, a steady-state variation of ±0.3–0.4°C results in a ±5% modeled change in $C_{V_{T,RH,N/L}}/C_{V_{std}}$ with N/L values of 0.46 to 4.6 m/h. In comparison, a steady-state change of ±2–2.5 percent RH causes 5 percent model variation at a constant T of 23°C. Thus, worst case errors in T and RH parameters among the ORNL and EPA data may have resulted in 1–2 percent errors due to variation in T and 5–10 percent errors due to variation in RH. Holding T and RH constant, variations of about ±6 to ±13 percent in N/L from standard values of 4.6 and 0.46 m/h, respectively, result in 5 percent changes in modeled $C_{V_{T,RH,N/L}}C_{V_{std}}$. Thus, worst case errors among the experimental N/L data may have resulted in about 2 percent variation in $C_{V_{T,RH,N/L}}/C_{V_{std}}$. Tight control and accurate calibration of T and RH parameters is clearly important for precise interlaboratory comparisons.

Table V. Linear regression analyses of the CH_2O emissions data fit to a single-compartment, single emitter model and Fick's Law.

A. Single-compartment single emitter model (Equation 1)

Laboratory	Slope ($m^2h/\mu g$)	Intercept ($m^3/\mu g$)	Corr. coef. (r)
EPA	0.0035 ± 0.0002	0.0039 ± 0.0005	0.99
ORNL	0.0040 ± 0.0004	0.0030 ± 0.0004	0.99
Combined	0.0039 ± 0.0001	0.0032 ± 0.0003	0.99

B. Mass transport model (Equation 2)

Laboratory	Slope (m/h)	Intercept ($\mu g/m^2h$)	Corr. coef. (r)
EPA	−0.72 ± 0.16	245 ± 22	0.88
ORNL	−0.73 ± 0.14	250 ± 19	0.91
Combined	−0.75 ± 0.12	252 ± 16	0.93

Conclusions

The CH_2O emissions of a selected particleboard underlayment sample have been compared by two laboratories in small-scale environmental chambers exercising tight control over measurement scheduling, design, and calibration. Intermethod discrepancies between two CEA instruments, a triple impinger/colorimetric analysis method and a DNPH sampler/chromatographic analysis method in two co-laboratory calibration sessions were typically <5–10 $\mu g/m^3$ against common sources of approximate 90 and 190 $\mu g/m^3$ CH_2O. Interlaboratory discrepancies in measured CH_2O concentration for particleboard emissions averaged about 10 $\mu g/m^3$. Such discrepancies are of similar or smaller magnitude than interspecimen variation in CH_2O emission strength. Interlaboratory variation in T, RH, and N/L are expected to account for <5–10 percent variation in measured CH_2O concentration, despite a strong sensitivity of CH_2O emission potential particularly to T and RH parameters.

Fitting the particleboard emissions data to a steady-state, single-compartment, single-emitter model supports a simple inverse proportionality between measured CH_2O concentration and N/L, despite fivefold variation in N and L values. Fitting the data to a linear mass transport model based on Fick's Law confirms the negative linear dependence of CH_2O emission rates on CH_2O concentration observed in prior studies. These results suggest that SSC experiments may incorporate convenient N and L values to avoid unreasonably low flow rates or test product areas with N/L levels that mimic indoor compartment scenarios. However, for sources demonstrating a Fick's Law dependence, the N/L may need to be adjusted to yield pollutant vapor concentrations consistent with real world levels.

Acknowledgment

Research at Oak Ridge National Laboratory sponsored by the U.S. Environmental Protection Agency under Interagency Agreement DW 89930762-01-4 under contract DE-AC05-840R21400 with the Martin Marietta Energy Systems Inc. Studies at Acurex Corporation supported by the U.S. Environmental Protection Agency Contract No. 68-02-3988. This work has not been subject to the Agency's peer and administrative review and, therefore, does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

References

1. T. G. Matthews, "Environmental chamber test methodology for organic vapors from solid emission sources," *Atmos. Environ.* **21**: 321 (1987).
2. R. A. Grot, S. Silberstein, K. Ishiguro, "Validation of Models for Predicting Formaldehyde Concentrations in Residences due to Pressed-Wood Products," National Bureau of Standards 85-3255, 1985.
3. D. Ackerman, "Quality Assurance Project Plan: Testing for Indoor Air Pollutants," Environmental Protection Agency, DCN #84-231-055-27-01, 1984.
4. M. S. Black, "Correlation of Wood Product Formaldehyde Emission Rates as Determined using a Large Scale Test Chamber, Small Scale Test Chamber and Formaldehyde Surface Emission Monitors," final report, prepared for the Formaldehyde Institute, 1985.
5. T. G. Matthews, T. J. Reed, B. J. Tromberg, C. R. Daffron, A. R. Hawthorne, "Formaldehyde Emissions from Combustion

Sources and Solid Formaldehyde-Resin-Containing Products: Potential Impact on Indoor Formaldehyde Concentrations," Advances in Chemistry Series No. 210, *Formaldehyde: Analytical Chemistry and Toxicology*, American Chemical Society, 1985, pp. 131-50.
6. G. E. Myers, M. Nagaoka, "Emission of formaldehyde by particleboard: effect of ventilation rate and loading on air-contamination levels," *Forest Products J.* **31**: 39 (1981).
7. G. E. Myers, "Effect of ventilation and board loading on formaldehyde concentration: a critical review of the literature," *Forest Products J.* **34**: 59 (1984).
8. J. J. Hoetjer, "Introduction to a Theoretical Model for the Splitting of Formaldehyde from Composition Board," report, Methanol Chemie Nederland, Delzijil, 1978.
9. T. G. Matthews, K. W. Fung, B. J. Tromberg, A. R. Hawthorne, "Surface emission monitoring of pressed-wood products containing urea-formaldehyde resins," *Environ. Int.* **12**: 301 (1986).
10. D. G. Sanchez, M. A. Mason, C. Norris, "Methods and results of characteristics of organic emission from indoor materials," *Atmos. Environ.* **21**: 337 (1986).
11. L. H. Nelms, M. A. Mason, B. A. Tichenor, "The Effects of Ventillation Rates and Product Loading on Organic Emission Rates from Particleboard," presented at the ASHRAE Meeting, Atlanta, GA, April 1986.
12. T. G. Matthews, "Evaluation of a modified CEA Instruments, Inc. Model 555 analyzer for the monitoring of formaldehyde vapor in domestic environments," *Am. Ind. Hyg. Assoc. J.* **43**: 547 (1982).
13. T. G. Matthews, T. J. Reed, B. J. Tromberg, C. R. Daffron, A. R. Hawthorne, "Modeling and Testing of Formaldehyde Emission Characteristics of Pressed-Wood Products: Reports XV, XVI and XVII to the U.S. Consumer Product Safety Commission," ORNL/TM-9104, Oak Ridge, TN, in press.
14. T. G. Matthews, A. R. Hawthorne, T. C. Howell, C. E. Metcalfe, R. B. Gammage, "Evaluation of selected monitoring methods for formaldehyde in domestic environments," *Environ. Int.* **8**: 143 (1982).
15. S. B. Tejada, "Evaluation of silica gel cartridges coated in situ with acidified 2,4-dinitrophenylhydrazine for sampling aldehydes and ketones in air," *Int. J. Environ. Anal. Chem.* **26**: 167 (1986).
16. C. S. Dudney, T. G. Matthews, W. G. Dreibelbus, A. R. Hawthorne, C. V. Thompson, K. P. Monar, J. L. Quillen, A. Hjelmfelt, "Indoor Pollutants in 70 Houses in the Tennessee Valley Area: Study Design and Measurement Methods," in *Proceedings of the 1986 EPA/APCA Symposium on Measurement of Toxic Air Pollutants*, APCA, Pittsburgh, PA, 1986.
17. T. G. Matthews, T. J. Reed, B. J. Tromberg, C. R. Daffron, K. W. Fung, C. V. Thompson, J. O. Simpson, A. R. Hawthorne, "Modeling and Testing of Formaldehyde Emission Characteristics of Pressed-Wood Products: Report XVIII to the U.S. Consumer Product Safety Commission," Oak Ridge National Laboratory, ORNL/TM-9867, Oak Ridge, TN, 1986.

T. G. Matthews and D. L. Wilson are with the Measurement Applications Group, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831. A. J. Thompson is currently with the University of Illinois, Urbana, IL 61801. M. A. Mason, S. N. Bailey, and L. H. Nelms are with the Environmental Systems Division, Acurex Corporation, Research Triangle Park, NC 27709. This paper was submitted for peer review September 12, 1986; the revised manuscript was received June 1, 1987.

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.